McAULAY NISSEN GOLDBERG & KIEL, LLP
Patent, Trademark and Copyright Matters

05-25-00

A

261 Madison Avenue
New York, NY 10016-2391
Phone: (212) 986-4090
Fax: (212) 818-9479
E-MAIL: MNGK-LAW.COM

JC830 U.S. PTO
05/24/00

TRANSMITTAL SHEET

EXPRESS MAIL No.: **EL 138 360 876 US**
Deposited: **May 24, 2000**
I hereby certify that this correspondence is being deposited with the United States Postal Service Express Mail under 37 CFR 1.10 on the date indicated above and is addressed to: Assistant Commissioner for Patents, Washington, DC 20231

/ **Ruth Montalvo**

JC583 U.S. PTO
09/577470
05/24/00

Assistant Commissioner for Patents
Washington, DC 20231

Date: **May 24, 2000**
Docket No: **JG-YY-4971**

Sir:

Transmitted herewith for filing is the Patent Application (37 CFR 1.53(b)) in the name(s) of:
Toshikazu HAMAMOTO, Akira UEKI, Koji ABE and Yasuo MATSUMORI

FOR: **NON-AQUEOUS ELECTROLYTIC SOLUTION AND LITHIUM SECONDARY BATTERY**

ENCLOSED ARE:

(X) 19 pages of Specification, 5 pages of Claims (# of claims 29) & Abstract;

( ) Figs. / ( ) sheet(s) of Drawings;

(X) Declaration and Power of Attorney;

(X) Assignment to: *Ube Industries, Ltd. with PTO-1619A*;

( ) Foreign priority(ies) of *Japanese Pat.Appln Nos. 11-143222 filed May 24, 1999 and 2000-116327 filed April 18, 2000*; the priority(ies) of which is(are) claimed under 35 USC 119; ***TO FOLLOW***

( ) Verified Statement to establish Small Entity Status (37 CFR 1.9 & 1.27):

( ) Information Disclosure Statement, PTO-1449 and ___ reference(s);

THE FILING FEE HAS BEEN CALCULATED AS SHOWN BELOW:

	Claims filed		Extra	SMALL $ 345.00	LARGE $ 690.00	**AMOUNT $ 690.00**
Total Claims	**29**	Minus 20	**9**	x $ 9.00	x $ 18.00	**$ 162.00**
Independent	**2**	Minus 03		x $ 39.00	x $ 78.00	**$ .00**
Multiple dependent claim fee				+ $ 130.00	+ $ 260.00	**$ .00**
Assignment recordation fee ($ 40.00):						**$ 40.00**
CHECK ENCLOSED:						**$ 892.00**

The Commissioner is hereby authorized to charge any additional fees associated with the filing of this application but not limited to: (X) Any patent application processing fees under 37 CFR 1.17
(X) Any filing fees under 37 CFR 1.16 for the presentation of extra claims
and any other fees required with this submission or to credit any overpayment to Deposit Account No. 13-0025.

Respectfully submitted

JEG:ram

Jules E. Goldberg - Reg. No. 24,408

00857470 . 052400

NON-AQUEOUS ELECTROLYTIC SOLUTION AND LITHIUM SECONDARY BATTERY

FIELD OF THE INVENTION

The present invention relates to a non-aqueous electrolytic solution favorably employable for a non-aqueous lithium secondary battery.

BACKGROUND OF THE INVENTION

At present, a non-aqueous secondary battery such as a lithium secondary battery (particularly, lithium ion secondary battery) is generally employed as an electric source for driving a small electronic device. The non-aqueous secondary battery comprises a positive electrode, a non-aqueous electrolytic solution, and a negative electrode. The non-aqueous lithium ion secondary battery preferably comprises a positive electrode of lithium complex oxide such as $LiCoO_2$, $LiMn_2O_4$, or $LiNiO_2$, a non-aqueous electrolytic solution such as a solution of electrolyte in a carbonate solvent such as ethylene carbonate (EC) or propylene carbonate (PC), and a negative electrode of carbonaceous material or lithium metal. Recently, the carbonaceous material such as coke or graphite has been paid much attention, because a negative electrode of carbonaceous material hardly forms thereon deposition of lithium metal in the form of dendrite and therefore hardly produces an electric short circuit with a positive electrode. Further, no liberation of lithium metal from the negative electrode occurs.

The non-aqueous secondary battery preferably has good battery characteristics such as large electric discharge capacity and high electric discharge retention. For instance, in a non-aqueous lithium ion secondary battery using a positive electrode of $LiCoO_2$, $LiMn_2O_4$, or

$LiNiO_2$, oxidative decomposition of a portion of the non-aqueous electrolytic solution undergoes in the electric charging stage. The decomposition product disturbs electrochemical reaction so that the electric discharge capacity decreases. It is considered that the oxidative decomposition takes place in the non-aqueous solvent of the non-aqueous electrolytic solution on the interface between the positive electrode and the electrolytic solution.

Moreover, in a non-aqueous lithium ion secondary battery using negative electrode of carbonaceous material of high crystallinity such as natural graphite or artificial (or synthetic) graphite, reductive decomposition of the solvent of the non-aqueous electrolytic solution undergoes on the surface of the negative electrode in the charging stage. The reductive decomposition on the negative electrode undergoes after repeated charging-discharging procedures even in the case of using a cyclic carbonate such as ethylene carbonate (EC) and propylene carbonate (PC) which is a preferably employed solvent of the electrolytic solution.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a non-aqueous electrolytic solution which is favorably employable for the preparation of a non-aqueous lithium secondary battery, particularly a non-aqueous lithium ion secondary battery.

It is another object of the invention to provide a non-aqueous secondary battery such as a lithium ion secondary battery which has improved discharge capacity retention.

The present invention resides in a non-aqueous electrolytic solution comprising at least two organic compounds dissolved in a solvent comprising a cyclic carbon-

ate and a chain carbonate, in an amount of 0.01 to 8 weight % (preferably, 0.1 to 4 weight %) for each organic compound,

in which both of said two organic compounds have a reduction potential higher those of the cyclic and chain carbonates, and

in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V (preferably less than 0.2 V).

In the non-aqueous electrolytic solution of the invention, the one organic compound preferably has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.05 V.

The invention further resides in a non-aqueous secondary battery which comprises a positive electrode comprising lithium complex oxide, a negative electrode comprising graphite, a non-aqueous electrolytic solution containing an electrolyte salt in a non-aqueous solvent, and a separator, in which the non-aqueous electrolytic solution comprises at least two organic compounds dissolved in a solvent comprising a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % (preferably, 0.1 to 4 weight %) for each compound, in which both of said two organic compounds have a reduction potential higher than those of the cyclic and chain carbonates, and in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V (preferably less than 0.2 V).

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in more detail.

The present invention is characterized by incorporation of at least two organic compounds into a solvent comprising a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % (preferably, 0.1 to 4 weight %) for each compound. Both of the two organic compounds have a reduction potential higher than those of the cyclic and chain carbonates, and one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V (preferably less than 0.2 V, more preferably less than 0.05 V).

The above-mentioned two or more organic compounds are preferably selected from the group consisting of a carbonate compound, a sultone compound, a sulfonate compound, a sulfone compound, and phenyl acetylene.

Examples of the carbonate compounds include vinylene carbonate, methyl propargyl carbonate, and benzaldoxime carbonate.

Examples of the sultone compounds include 1,3-propanesultone and 1,4-butanesultone.

Examples of the sulfonate compounds include 1,4-butanediol dimethane sulfonate and ethylene glycol dimethane sulfonate.

Examples of the sulfone compounds include divinyl sulfone.

The two or more organic compounds are preferably employed in such manner that one organic compound is a carbonate compound, and another organic compound is a sultone compound, a sulfonate compound, or a sulfone compound. Particularly, it is preferred that one organic compound is vinylene carbonate or methyl propargyl carbonate, and another organic compound is 1,3-propanesul-

tone, 1,4-butanesultone, 1,4-butanediol dimethane sulfonate, or ethylene glycol dimethane sulfonate. It is also preferred that one organic compound is benzaldoxime methylcarbonate and another organic compound is divinylsulfone. It is also preferred that one organic compound is a sulfonate compound and another organic compound is a sultone compound. It is also preferred that one organic compound is 1,4-butanediol dimethanesulfonate or ethylene glycol dimethanesulfonate, and another organic compound is 1,3-propanesultone or 1,4-butanesultone. It is also preferred that one organic compound is phenylacetylene, and another organic compound is vinylene carbonate, 1,3-propanesultone, or 1,4-butanesultone.

It is preferred that the addition of the above-described two or more organic compounds is made to a non-aqueous solvent comprising one or more cyclic carbonates and one or more chain carbonates. Examples of the cyclic carbonates include ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC). Examples of the chain carbonates include dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl ethyl carbonate (MEC), and methyl isopropyl carbonate (MIPC). Other known non-aqueous solvents such as tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,2-dibutoxyethane, γ-butyrolactone, acetonitrile, methyl propionate, and dimethylformamide may be incorporated into the mixture of the cyclic carbonate and the chain carbonate. The mixture solvent of the non-aqueous electrolytic solution preferably contains the combination of the cyclic carbonate and chain carbonate at least 60 weight %, more preferably at least 80 weight %, and most preferably at least 90 weight %. In the non-aqueous solvent mixture and in the combination of the cyclic carbonate and the chain carbonate, the cyclic carbonate preferably is in an amount of 5 to 70 volume %, and the chain carbonate preferably is in an amount of 95

to 30 volume %.

In the non-aqueous electrolytic solution of the invention, the combined two or more organic compounds having a reduction potential higher than the non-aqueous solvent are considered to function in the following manner.

In the electric charging stage, the combined organic compounds having a high reduction potential decomposes on the surface of a negative electrode almost at the same time or with a short interval, prior to the decomposition of the solvent material. The products produced by the decomposition of the organic compounds (i.e., additives) deposits on the surface of the negative electrode to cover the surface with an inactive material, which reduces decomposition of the solvent material. If the amount of the additive is larger than a certain level, however, the function of the electrolytic solution lowers.

The non-aqueous electrolytic solution preferably comprises further an electrolyte salt (particularly, inorganic electrolyte salt) such as $LiPF_6$, $LiBF_4$, $LiClO_4$, CF_3SO_2Li, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, $LiC(SO_2CF_3)_3$, $LiPF_4(CF_3)_2$, $LiPF_3(CF_3)_3$, $LiPF_3(C_2F_5)_3$, $LiPF_5$(iso-C_3F_7), and $LiPF_4$(iso-$C_3F_7)_2$. The electrolyte salts can be employed singly or in combination. Generally, the electrolyte salt can be incorporated into the non-aqueous solvent in such an amount to give an electrolytic solution of 0.1M to 3M, preferably 0.5M to 1.5M.

The non-aqueous secondary battery of the invention comprises a positive electrode and a negative electrode in addition to the non-aqueous electrolytic solution.

The positive electrode generally comprises a positive electrode active material and an electro-conductive binder composition.

The positive electrode active material preferably is a complex metal oxide containing at least one metal element selected from the group consisting of cobalt, manga-

nese, nickel, chromium, iron, and vanadium and a lithium element. Examples of the complex metal oxides include $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$.

The electro-conductive binder composition can be produced by a mixture of an electro-conductive material such as acetylene black or carbon black, a binder such as polytetrafluoroethylene (PTFE) or poly(vinylidene fluoride) (PVDF), and a solvent. For the preparation of a positive electrode, the mixture is coated on a metal plate such as aluminum foil or stainless plate, dried, and pressed for molding. The molded product is then heated *in vacuo* at a temperature of approx. 50 to 250°C for approx. 2 hours, to give the desired positive electrode.

The negative electrode comprises a negative electrode active material such as a lithium metal, a lithium alloy, carbonaceous material having a graphite-type crystalline structure which can absorb and release lithium ion, or a complex tin oxide. Examples of the carbonaceous materials include thermally decomposed carbonaceous materials, cokes, graphites (e.g., artificial graphite and natural graphite), fired organic polymer materials, and carbon fibers. Preferred are carbonaceous materials having a graphite-type crystalline structure in which the lattice distance of lattice surface (002), namely, d_{002}, is in the range of 0.335 to 0.340 nm. The negative electrode active material in the powdery form such as carbonaceous powder is preferably used in combination with a binder such as ethylene propylene diene terpolymer (EPDM), polytetrafluoroethylene (PTFE) or poly(vinylidene fluoride) (PVDF).

There are no specific limitations with respect to the structure of the non-aqueous secondary battery of the invention. For instance, the non-aqueous secondary battery can be a battery of coin type comprising a positive electrode, a negative electrode, and single or plural

separators, or a cylindrical or prismatic battery comprising a positive electrode, a negative electrode, and a separator roll. The separator can be a known microporous polyolefin film, woven fabric, or non-woven fabric.

The present invention is further described by the following non-limiting examples.

[Measurement of Reduction Potential]

Ten mg of graphite powder (MCMB6-28, produced by Osaka Gas Chemical Co., Ltd.) is mixed with 10 wt.% of polyvinylidene fluoride (binder). The mixture is placed in N-methylpyrrolidone to give a slurry. The slurry is coated on a electro-collector stainless steel plate (surface area: 2 cm^2). Thus coated plate is set as a working electrode to form a triode cell in combination with counter and reference electrodes using lithium metal.

A non-aqueous solvent is prepared from ethylene carbonate and methyl ethyl carbonate at a volume ratio of 3:7. To the solvent is added $LiPF_6$ (electrolyte, to give 1 M concentration) to produce an electrolytic solution. To the resulting electrolytic solution is added an organic compound (i.e., additive) to be measured, in an amount of 2 wt.%.

The triode cell is placed in the additive-containing electrolytic solution, and the reduction potential is measured at room temperature under a potential scanning rate of 1 mV/sec. A potential in terms of V at which a current of 0.5 mA flows is assigned to the reduction potential.

The reduction potentials measured on various organic compounds are set forth in Table 1.

Table 1

Organic Compound (Additive)	Abbr.	Reduction Potential (vs. lithium metal)
Vinylene carbonate	VC	0.81 V
1,3-Propanesultone	PS	0.83 V
1,4-Butanesultone	BS	0.80 V
1,4-Butanediol dimethane sulfonate	BDDMS	0.81 V
Ethylene glycol dimethane sulfonate	EGDMS	0.81 V
Methyl propargyl carbonate	MPGC	0.82 V
Phenylacetylene	PA	0.81 V
Benzaldoxime carbonate	BAOMC	1.78 V
Divinylsulfone	VS	1.45 V

[Example 1]

1) Preparation of non-aqueous electrolytic solution

In a non-aqueous mixture of propylene carbonate and dimethyl carbonate [PC:DMC=1:2, volume ratio] was dissolved $LiPF_6$ to give a non-aqueous electrolytic solution of 1 M concentration. To the electrolytic solution were added vinylene carbonate (VC) and 1,3-propanesultone (PS), both in an amount of 1.5 wt.% (based on the amount of the electrolytic solution).

2) Preparation of lithium secondary battery and measurement of its battery characteristics

$LiCoO_2$ (positive electrode active material, 80 wt.%), acetylene black (electro-conductive material, 10 wt.%), and poly(vinylidene fluoride) (binder, 10 wt.%) were mixed. To the resulting mixture was further added N-methylpyrrolidone (solvent). Thus produced positive electrode mixture was coated on aluminum foil, dried, molded under pressure, and heated to give a positive

electrode.

Natural graphite (negative electrode active material, 90 wt.%) and poly(vinylidene fluoride) (binder, 10 wt.%) were mixed. To the resulting mixture was further added N-methylpyrrolidone (solvent). Thus produced negative electrode mixture was coated on copper foil, dried, molded under pressure, and heated to give a negative electrode.

The positive and negative electrodes, a microporous polypropylene film separator, and the non-aqueous electrolytic solution were combined to give a coin-type battery (diameter: 20 mm, thickness: 3.2 mm).

The coin-type battery was charged at room temperature (20°C) with a constant electric current (0.8 mA) to reach 4.2 V, and then the charging was continued under a constant voltage of 4.2 V for a period of 6 hours. Subsequently, the battery was discharged to give a constant electric current (0.8 mA). The discharge was continued to give a terminal voltage of 2.7 V. The charge-discharge cycle was repeated 50 times.

The initial discharge capacity was as much as 0.97 which was calculated on the basis that the initial discharge capacity measured in Comparison Example 6 (using a solvent mixture consisting of ethylene carbonate, propylene carbonate and diethyl carbonate, 3/1/6, volume ratio) was set to 1.

After the 50 cycle charge-discharge procedure, the discharge capacity was 94.8% of the initial discharge capacity. No deformation was observed on the battery appearance. The low temperature characteristics were satisfactory.

The preparation and evaluation of the battery are summarized in Table 2.

[Comparison Example 1]

The procedures of Example 1 were repeated except

that neither VC nor PS were incorporated into the electrolytic solution.

In performing the charging procedure using the secondary battery, propylene carbonate (PC) decomposed at the first charging procedure, and no discharge was done. The battery was deformed. The battery was then disjointed to examine its interior. The graphite negative electrode showed exfoliation on its surface.

The preparation and evaluation of the battery are summarized in Table 2.

[Comparison Examples 2 to 5]

The procedures of Example 1 were repeated except that only one of VC and PS was incorporated into the electrolytic solution.

The preparation and evaluation of the battery are summarized in Table 2.

Table 2
(Solvent: PC/DMC=1/2)

Example	Additive(s) (%)	Initial discharge capacity (relative value)	Discharge capacity retention
Example 1	VC(1.5)/PS(1.5)	0.97	94.8%
Com.Ex. 1	None	0	--
Com.Ex. 2	VC(1.5)	0.93	83.2%
Com.Ex. 3	VC(3.0)	0.95	84.8%
Com.Ex. 4	PS(1.5)	0.95	82.7%
Com.Ex. 5	PS(3.0)	0.96	84.3%

[Examples 2 & 3]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/DEC (1/2) (for Example 2), and that the solvent was replaced with EC/MEC (1/2) and the negative electrode was made from artificial graphite (for Example 3).

The preparation and evaluation of the battery are summarized in Table 3.

Table 3
(Additive: VC(1.5%)/PS(1.5%))

Example	Solvent (graphite)	Initial discharge capacity (relative value)	Discharge capacity retention
Example 2	EC/DEC=1/2 (natural)	1.02	95.3%
Example 3	EC/MEC=1/2 (artificial)	1.03	94.7%

[Examples 4 to 7]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (1/1/2) and that the amount of the added organic compounds were changed.

The preparation and evaluation of the battery are summarized in Table 4.

Table 4
(Solvent: EC/PC/DEC=1/1/2)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 4	VC(0.5)/PS(1.5)	1.01	93.5%
Example 5	VC(3.0)/PS(1.5)	0.98	93.8%
Example 6	VC(1.5)/PS(0.5)	1.00	93.1%
Example 7	VC(1.5)/PS(3.0)	0.99	93.6%

[Examples 8 and Comparison Examples 6 to 9]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additives was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 5.

Table 5
(Solvent: EC/PC/DEC=3/1/6,
Negative electrode: artificial graphite)

Example	Additives	Initial dis-charge capacity (relative value)	Discharge capacity retention
Example 8	VC(1.5)/PS(1.5)	1.02	95.5%
Com.Ex. 6	None	1.00	81.6%
Com.Ex. 7	VC(1.5)	0.97	83.8%
Com.Ex. 8	PS(1.5)	1.00	84.2%
Com.Ex. 9	VC(10.0)/PS(10.0)	0.93	80.6%

[Example 9]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/MEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

Each of the additives of VC and PS were incorporated in an amount of 2.0 wt.%.

The preparation and evaluation of the battery are summarized in Table 6.

Table 6
(Solvent: EC/PC/MEC=3/1/6,
Negative electrode: artificial graphite)

Example	Additives	Initial dis-charge capacity (relative value)	Discharge capacity retention
Example 9	VC(2.0)/PS(2.0)	1.03	94.1%

[Example 10]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DMC/MIPC (3/1/3/3) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The preparation and evaluation of the battery are summarized in Table 7.

Table 7
(Solvent: EC/PC/DMC/MIPC (3/1/3/3),
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 10	VC(1.5)/PS(1.5)	1.01	93.4%

[Examples 11 & 12 and Comparison Example 10]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DMC/DEC (3/1/3/3), that $LiCoO_2$ (positive electrode active material) was replaced with $LiMn_2O_4$, and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 8.

Table 8
(Solvent: EC/PC/DMC/DEC (3/1/3/3),
Positive electrode: $LiMn_2O_4$,
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 11	VC(1.5)/PS(1.5)	1.05	95.5%
Example 12	VC(1.5)/BS(1.5)	1.05	95.3%
Com.Ex. 10	BS(1.5)	1.00	83.4%

[Examples 13 to 19 and Comparison Examples 11 to 14]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 9.

Table 9
(Solvent: EC/PC/DEC (3/1/6),
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 13	VC(1.5)/PS(1.0)/BS(0.5)	1.03	95.8%
Example 14	VC(1.5)/BDDMS(1.5)	1.02	94.2%
Example 15	VC(1.5)/EGDMS(1.5)	1.01	93.7%
Example 16	VC(1.5)/BDDMS(1.0)/EGDMS(0.5)	1.02	94.9%
Example 17	PS(1.5)/BDDMS(1.5)	1.00	93.9%
Example 18	PS(1.5)/EGDMS(1.5)	1.00	93.3%
Example 19	PS(1.5)/BDDMS(1.0)/EGDMS(0.5)	1.01	94.5%
Com.Ex. 11	BDDMS(1.5)	1.01	82.9%
Com.Ex. 12	EGDMS(1.5)	1.01	82.3%
Com.Ex. 13	BDDMS(3.0)	1.01	83.9%
Com.Ex. 14	EGDMS(3.0)	1.01	83.1%

[Examples 20 to 25 and Comparison Examples 15 to 18]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 10.

Table 10
(Solvent: EC/PC/DEC (3/1/6),
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 20	VC(1.5)/MPGC(1.5)	1.00	92.3%
Example 21	VC(1.5)/PA(1.5)	1.00	91.5%
Example 22	VC(1.5)/MPGC(0.5) /PA(1.0)	1.01	92.9%
Example 23	PS(1.5)/MPGC(1.5)	1.01	92.0%
Example 24	PS(1.5)/PA(1.5)	1.01	90.9%
Example 25	PS(1.5)/MPGC(0.5) /PA(1.0)	1.02	92.5%
Com.Ex. 15	MPGC(1.5)	1.00	82.0%
Com.Ex. 16	PA(1.5)	1.00	81.9%
Com.Ex. 17	MPGC(3.0)	1.00	83.2%
Com.Ex. 18	PA(3.0)	1.00	82.9%

[Examples 26 to 28 and Comparison Examples 19 to 25]

The procedures of Example 1 were repeated except that the solvent was replaced with EC/PC/DEC (3/1/6) and that the natural graphite for the negative electrode was replaced with artificial graphite.

The incorporation of the additive(s) was examined under various conditions.

The preparation and evaluation of the battery are summarized in Table 11.

Table 11
(Solvent: EC/PC/DEC (3/1/6),
Negative electrode: artificial graphite)

Example	Additives	Initial discharge capacity (relative value)	Discharge capacity retention
Example 26	VS(0.15)/BAOMC(2.0)	1.01	93.8%
Example 27	VS(0.2)/BAOMC(1.5)	1.00	94.0%
Example 28	VS(0.3)/BAOMC(1.5)	1.00	92.5%
Com.Ex. 19	VS(0.2)	1.00	83.5%
Com.Ex. 20	BAOMC(1.5)	1.00	83.2%
Com.Ex. 21	VS(1.7)	0.77	74.7%
Com.Ex. 22	BAOMC(1.7)	0.99	85.1%
Com.Ex. 23	VS(10.0)/BAOMC(10.0)	0.66	63.4%
Com.Ex. 24	BDDMS(1.5)/BAOMC(1.5)	1.00	83.2%
Com.Ex. 25	PA(1.5)/VS(0.2)	1.00	83.5%

WHAT IS CLAIMED IS:

1. A non-aqueous electrolytic solution comprising at least two organic compounds dissolved in a solvent comprising a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % for each compound,

in which both of said two organic compounds have a reduction potential higher than those of the cyclic and chain carbonates, and

in which one of the organic compounds has a reduction potential equal to that of another organic compound or has a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V.

2. The non-aqueous electrolytic solution of claim 1, in which each organic compound is dissolved in the solvent in an amount of 0.1 to 4 weight %.

3. The non-aqueous electrolytic solution of claim 1, in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.2 V.

4. The non-aqueous electrolytic solution of claim 3, in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.05 V.

5. The non-aqueous electrolytic solution of claim 1, in which said one organic compound is a carbonate compound and another organic compound is a sultone compound, a sulfonate compound, or a sulfone compound.

6. The non-aqueous electrolytic solution of claim 5, in which said one organic compound is vinylene carbonate or methyl propargyl carbonate and another organic compound is 1,3-propanesultone, 1,4-butanesultone, 1,4-butanediol dimethane sulfonate, or ethylene glycol dimethane sulfonate.

7. The non-aqueous electrolytic solution of claim 5, in which said one organic compound is benzaldoxime methylcarbonate and another organic compound is divinylsulfone.

8. The non-aqueous electrolytic solution of claim 1, in which said one organic compound is a sulfonate compound and another organic compound is a sultone compound.

9. The non-aqueous electrolytic solution of claim 8, in which said one organic compound is 1,4-butanediol dimethanesulfonate or ethylene glycol dimethane sulfonate, and another organic compound is 1,3-propanesultone or 1,4-butanesultone.

10. The non-aqueous electrolytic solution of claim 1, in which said one organic compound is phenylacetylene, and another organic compound is vinylene carbonate, 1,3-propanesultone, or 1,4-butanesultone.

11. The non-aqueous electrolytic solution of claim 1, in which the solvent comprises 5 to 70 volume % of the cyclic carbonate and 95 to 30 volume % of the chain carbonate.

12. The non-aqueous electrolytic solution of claim 1, in which the cyclic carbonate is selected from the group consisting of ethylene carbonate, propylene carbonate, and butylene carbonate.

13. The non-aqueous electrolytic solution of claim 1, in which the chain carbonate is selected from the group consisting of dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, and methyl isopropyl carbonate.

14. The non-aqueous electrolytic solution of claim 1, which contains an electrolyte salt.

15. A non-aqueous lithium secondary battery which comprises a positive electrode comprising lithium complex oxide, a negative electrode comprising graphite, a non-aqueous electrolytic solution containing an electrolyte salt in a non-aqueous solvent, and a separator, in which the non-aqueous electrolytic solution comprises at least two organic compounds dissolved in a solvent comprising a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % for each compound, in which both of said two organic compounds have a reduction potential higher than those of the cyclic and chain carbonates, and in which one of the organic compounds has a reduction potential equal to that of another organic compound or has a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V.

16. The non-aqueous lithium secondary battery of claim 15, in which each organic compound is dissolved in the solvent in an amount of 0.1 to 4 weight %.

17. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.2 V.

18. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound has a reduction potential equal to that of another organic compound or a reduction potential lower or higher than that of another organic compound by a potential of less than 0.05 V.

19. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound is a carbonate compound and another organic compound is a sultone compound, a sulfonate compound, or a sulfone compound.

20. The non-aqueous lithium secondary battery of claim 19, in which said one organic compound is vinylene carbonate or methyl propargyl carbonate and another organic compound is 1,3-propanesultone, 1,4-butanesultone, 1,4-butanediol dimethanesulfonate, or ethylene glycol dimethane sulfonate.

21. The non-aqueous lithium secondary battery of claim 19, in which said one organic compound is benzaldoxime methylcarbonate and another organic compound is divinyl sulfone.

22. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound is a sulfonate compound and another organic compound is a sultone compound.

23. The non-aqueous lithium secondary battery of claim 22, in which said one organic compound is 1,4-butanediol dimethanesulfonate or ethylene glycol dimethane sulfonate, and another organic compound is 1,3-propanesultone or 1,4-butanesultone.

24. The non-aqueous lithium secondary battery of claim 15, in which said one organic compound is phenyl-acetylene, and another organic compound is vinylene carbonate, 1,3-propanesultone, or 1,4-butanesultone.

25. The non-aqueous lithium secondary battery of claim 15, in which the solvent comprises 5 to 70 volume % of the cyclic carbonate and 95 to 30 volume % of the chain carbonate.

26. The non-aqueous lithium secondary battery of claim 15, in which the cyclic carbonate is selected from the group consisting of ethylene carbonate, propylene carbonate, and butylene carbonate.

27. The non-aqueous lithium secondary battery of claim 15, in which the chain carbonate is selected from the group consisting of dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, and methyl isopropyl carbonate.

28. The non-aqueous secondary battery of claim 15, in which said graphite is natural graphite or artificial graphite.

29. The non-aqueous secondary battery of claim 15, in which the graphite has a lattice plane of (002) having a plane distance in term of d_{002} in a length of 0.335 to 0.340 nm.

ABSTRACT OF THE DISCLOSURE

A non-aqueous electrolytic solution composed of two or more organic compounds dissolved in a solvent composed of a cyclic carbonate and a chain carbonate, in an amount of 0.01 to 8 weight % for each compound, in which both of the two organic compounds have a reduction potential higher than those of the cyclic and chain carbonates, and in which one of the organic compounds has a reduction potential equal to that of another organic compound or has a reduction potential lower or higher than that of another organic compound by a potential of less than 0.4 V is favorably employable for a non-aqueous secondary battery.

Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。	As a below named inventor, I hereby declare that:
私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。	My residence, post office address and citizenship are as stated next to my name.
下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。	I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
______________	NON-AQUEOUS ELECTROLYTIC SOLUTION AND LITHIUM SECONDARY BATTERY
上記発明の明細書（下記の欄でx印がついていない場合は、本書に添付）は、	the specification of which is attached hereto unless the following box is checked:
☐ __月__日に提出され、米国出願番号または特許協定条約国際出願番号を__________とし、（該当する場合）__________に訂正されました。	☐ was filed on __________ as United States Application Number or PCT International Application Number __________ and was amended on __________ (if applicable).
私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。	I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.
私は、連邦規則法典第３７編第１条５６項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。	I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration
(日本語宣言書)

私は、米国法典第３５編１１９条(a)-(d)項又は３６５条(b)項に基き下記の、米国以外の国の少なくとも一ヵ国を指定している特許協力条約３６５(a)項に基ずく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)
外国での先行出願

(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願年月日)	Priority Not Claimed 優先権主張なし
11-143222	Japan	24/05/1999	☐
2000-116327	Japan	18/04/2000	☐
			☐
			☐

私は、第３５編米国法典１１９条(e)項に基いて下記の米国特許出願規定に記載された権利をここに主張いたします。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.) (出願番号)	(Filing Date) (出願日)

(Application No.) (出願番号)	(Filing Date) (出願日)

私は、下記の米国法典第３５編１２０条に基いて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約３６５条(c)に基ずく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第３５編１１２条第１項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第３７編１条５６項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Application No.) (出願番号)	(Filing Date) (出願日)	(Status: Patented, Pending, Abandoned) (現況：特許許可済、係属中、放棄済)

私は、私自身の知識に基ずいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じるところに基ずく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第１８編第１００１条に基ずき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration
(日本語宣言書)

委任状：　私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行し、本出願に関するヤナガワ・アンド・カンパニーからの指示を受ける弁理士または代理人として、下記の者を指名いたします。（弁護士、または代理人の氏名及び登録番号を明記のこと）

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith and to take instructions in connection therewith from Yanagawa & Company (list name and registration number)

Lloyd McAulay, Reg. No. 20,423
J.Harold Nissen, Reg. No. 17,283
Jules E. Goldberg., Reg. No. 24,408
Gerald H. Kiel, Reg. No. 25,116
Frank Hand, Reg. No. 22,280

Eugene LeDonne, Reg. No. 35,930
Mark Montague, Reg. No. 36,612
Stephen M. Chin, Reg. No. 39,938
F. Aaron Dubberley, Reg. No. 41,001

書類送付先

Send Correspondence to:

Jules E. Goldberg
McAulay Nissen Goldberg Kiel & Hand LLP
261 Madison Avenue, New York, NY 10016-2391

直接電話連絡先：（名前及び電話番号）

Direct Telephone Calls to: *(name and telephone number)*

Jules E. Goldberg, Esq.
Tel. (212) 986-4090

唯一または第一発明者名	Full name of sole or first inventor Toshikazu Hamamoto
発明者の署名　日付	Inventor's signature Toshikazu Hamamoto　Date May 10, 2000
住所	Residence Ube-shi, Yamaguchi, Japan
国籍	Citizenship Japan
私書箱	Post Office Address c/o Ube Research Laboratory, Ube Industries, Ltd., 1978-5, Oaza Kogushi, Ube-shi, Yamaguchi, 755-8633 Japan
第二共同発明者	Full name of second joint inventor, if any Akira Ueki
第二共同発明者　日付	Second inventor's signature Akira Ueki　Date May 10, 2000
住所	Residence Ube-shi, Yamaguchi, Japan
国籍	Citizenship Japan
私書箱	Post Office Address c/o Ube Research Laboratory, Ube Industries, Ltd., 1978-5, Oaza Kogushi, Ube-shi, Yamaguchi, 755-8633 Japan

（第三以降の共同発明者についても同様に記載し、署名をすること）

(Supply similar information and signature for third and subsequent joint inventors.)

Japanese Language Declaration
(日本語宣言書)

委任状： 私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行し、本出願に関するヤナガワ・アンド・カンパニーからの指示を受ける弁理士または代理人として、下記の者を指名いたします。（弁護士、または代理人の氏名及び登録番号を明記のこと）

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith and to take instructions in connection therewith from Yanagawa & Company (list name and registration number)

Lloyd McAulay, Reg. No. 20,423
J.Harold Nissen, Reg. No. 17,283
Jules E. Goldberg., Reg. No. 24,408
Gerald H. Kiel, Reg. No. 25,116
Frank Hand, Reg. No. 22,280

Eugene LeDonne, Reg. No. 35,930
Mark Montague, Reg. No. 36,612
Stephen M. Chin, Reg. No. 39,938
F. Aaron Dubberley, Reg. No. 41,001

書類送付先

Send Correspondence to:

Jules E. Goldberg
McAulay Nissen Goldberg Kiel & Hand LLP
261 Madison Avenue, New York, NY 10016-2391

直接電話連絡先：（名前及び電話番号）

Direct Telephone Calls to: *(name and telephone number)*

Jules E. Goldberg, Esq.
Tel. (212) 986-4090

第三共同発明者	Full name of third joint inventor, if any Koji Abe
第三共同発明者 日付	Third inventor's signature Koji Abe Date May 10, 2000
住所	Residence Ube-shi, Yamaguchi, Japan
国籍	Citizenship Japan
私書箱	Post Office Address c/o Ube Research Laboratory, Ube Industries, Ltd., 1978-5, Oaza
	Kogushi, Ube-shi, Yamaguchi, 755-8633 Japan
第四共同発明者	Full name of fourth joint inventor, if any Yasuo Matsumori
第四共同発明者 日付	Fourth inventor's signature Yasuo Matsumori Date May 10, 2000
住所	Residence Ube-shi, Yamaguchi, Japan
国籍	Citizenship Japan
私書箱	Post Office Address c/o Ube Research Laboratory, Ube Industries, Ltd., 1978-5, Oaza
	Kogushi, Ube-shi, Yamaguchi, 755-8633 Japan

（第三以降の共同発明者についても同様に記載し、署名をすること）

(Supply similar information and signature for third and subsequent joint inventors.)